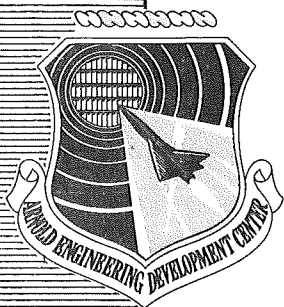


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A STUDY OF VACUUM CRYOSORPTION BY ACTIVATED CHARCOAL

By

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Aerospace Environmental Facility
ARO, Inc.**

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A STUDY OF VACUUM CRYOSORPTION
BY ACTIVATED CHARCOAL

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Aerospace Environmental Facility
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a subsidiary of Sverdrup and Parcel, Inc.

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ABSTRACT

An experimental program was carried out in the 10^{-8} to 10^{-2} -torr region to supply basic information on the adsorption of noncondensable gases at 77°K and to establish the functional dependence of adsorption rate on pressure and amount of gas adsorbed. From the experimental results, analytical expressions are developed which describe the behavior of adsorption rate in terms of the adsorption parameters for high vacuum, low temperature conditions. These expressions are shown to agree with the observed pressure-time variations resulting from charcoal adsorption provided the charcoal remains well below saturation.

PUBLICATION REVIEW

This report has been reviewed and publication is approved.



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NOMENCLATURE

A	Projected area of charcoal bed
A_i	Area of the i^{th} enveloping surface
C	Flow rate dependent constant of pressure-time relation
D	Volumetric rate of desorption
$(\frac{dv}{dt})_a$	Volumetric flow rate at 293°K and 760 mm pressure
$(\frac{dv}{dt})_E$	Volumetric exhaust rate at chamber conditions
E	Volumetric exhaust rate
k	Adsorption constant
M	Molecular mass
P	Gas pressure
P_a	Standard atmosphere pressure (760 mm)
P_s	Base pressure of conventional pump
P_∞	Equilibrium gas pressure
Q	Throughput
Q_{ad}	Fraction of throughput adsorbed
R	Universal gas constant
S	Volumetric adsorption rate
S^*	Speed of pump
T^*	Statistically weighted gas temperature
T_a	Ambient atmosphere temperature (293°K)
T_c	Chamber gas temperature
T_i	Temperature of the i^{th} enveloping surface
t	Time
V_{ad}	Volume (amount) of gas adsorbed
V_{ad}^*	Volume of gas not adsorbed (defined by Eq. (39))
V_c	Volume of chamber

α	Sticking fraction
δ	Fraction of throughput not adsorbed
ζ	Isotherm constant

1.0 INTRODUCTION

In earlier charcoal adsorption studies performed at the Arnold Engineering Development Center (AEDC), Air Force Systems Command (AFSC), the volumetric rate of nitrogen gas adsorption by charcoal was experimentally indicated to be inversely proportional to the gas pressure (Ref. 1). The gas pressure, in turn, was shown to be directly proportional to the amount of gas adsorbed (Refs. 1 and 2). In Ref. 1, analytical expressions for the rate of adsorption and pressure-time relation were derived from definitions of three constants (generally referred to as the adsorption parameters). It was then suggested that the rate of adsorption could be dependent only on amount of gas adsorbed and independent of pressure. At the conclusion of that research program, it was recognized that by proving the pressure independence of volumetric adsorption rate, analytical expressions for the complete adsorption process would result.

A subsequent program of research on charcoal adsorption was undertaken with the following three objectives: (1) to measure the adsorption parameters for gases other than nitrogen; (2) to experimentally verify the pressure independence of volumetric rate of adsorption; and (3) to obtain analytical expressions for the rate of adsorption, rate of desorption, and rate of exhaust (rate of gas removal).

The first objective was achieved by using the interrupted flow technique (Ref. 1) on a number of different gases to determine the adsorption parameters for each gas. The vacuum chamber used for these measurements was similar to that reported in Ref. 1 except that this chamber was immersed in liquid nitrogen for greater temperature stability.

In order to accomplish the second objective, it was necessary to establish the experimental condition of being able to independently vary both the amount of gas adsorbed and the pressure before making a rate measurement. This was done by using a divided vacuum chamber - one section of which contained charcoal. Before each run, the desired pressure level was obtained in one section, and the initial amount of gas adsorbed was obtained for the charcoal in the charcoal section. When the desired initial conditions for a rate measurement were obtained, the two sections were suddenly exposed to each other.

The third objective, analytical expressions for rate of adsorption, desorption, and exhaust, was accomplished by comparing the rate of

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adsorption to the pumping speed of a conventional pump while retaining the conventional meaning of exhaust rate. In regard to this description, an anomalous behavior was found to exist in the analytical description of all three rates for small amounts of gas adsorbed. A suggested correction is presented which is shown to agree with experimental data and from which a new pressure-time relation is derived that contains a description of the transient region between onset of inleakage and establishment of a steady pressure rise.

2.0 APPARATUS

This study was conducted in two different vacuum systems. Each system was designed to obtain a particular type of information.

2.1 VACUUM CHAMBERS

The first chamber was actually two chambers joined together. The main chamber was a closed cylinder, 16 in. in diameter by 32 in. long. The other chamber was a 6-in. -diam elbow terminated with a small steel pot. The elbow chamber and main chamber were joined by an air-operated 6-in. sliding gate valve. A high-speed diffusion pump and a gas addition system were attached to the main chamber. Charcoal was contained in the elbow pot which in turn was immersed in a container of liquid nitrogen. All other walls were at room temperature. A liquid-nitrogen-cooled baffle at the elbow-pot junction served to cool any gas flowing into the pot. The nominal volume of the main chamber was 115 liters and that of the elbow was 12.4 liters. The pressure of each chamber was monitored and recorded continuously. This chamber, a schematic of which is shown in Fig. 1, will be referred to as the 16-in. cell in the remainder of this report.

The second chamber, shown in Fig. 2, was similar to a steel bell jar. Charcoal was installed in a holder on the base plate, and the whole assembly was immersed in liquid nitrogen. A nude ion gage was installed internally. Ion gage, heater, and thermocouple leads were brought out of the system through a steel pipe which projected up and out of the liquid nitrogen. This system will be referred to as the cold wall cell. The nominal volume of the cold wall cell was 14.5 liters.

2.2 GAS ADDITION SYSTEM

Both systems had the same type of gas addition system. An example of this system is shown schematically in Fig. 2. Commercial standard leaks were used to meter the gas flow. During flow-off time, the flow line was pumped to forepump pressure on both sides of the standard leak. Pressure surges on opening the flow line to the high vacuum system were negligible because of the small volume of the flow line. This particular arrangement provided a means for interrupting the gas flow to the vacuum system. Approximately 30 sec were required to evacuate the flow line after flow termination, but this presented no problem because in most cases the vacuum system required more time than this to return to equilibrium.

2.3 RECORDING EQUIPMENT

Commercial ion gages were used as pressure monitors on all systems. The output of each ion gage control unit was fed to a millivolt recorder, and continuous pressure-time curves were recorded for each experiment. Thermocouple outputs were fed to multipoint millivolt recorders, permitting simultaneous, continuous, temperature-time recording of several different thermocouples during each experiment.

3.0 PROCEDURE

3.1 GENERAL PROCEDURE

The procedure of operation in the cold wall cell was to first evacuate the chamber to a low pressure (10^{-4} torr) at room temperature. Then, the system was flushed with helium and isolated while containing a helium pressure of about 200 microns. Liquid nitrogen coolant was then introduced, and the chamber was thus left to cool for from one to two hours. Helium was used because it is not adsorbed by charcoal. As the charcoal cooled, residual gases other than helium were adsorbed, and when the helium was removed after the charcoal temperature had reduced to 77°K, the chamber pressure dropped to the low 10^{-8} -torr or high 10^{-9} -torr region. The chamber base pressure was limited by the amount of residual gases adsorbed, and this was determined by the amount of adsorbable gas remaining (and outgassed from warm charcoal) in the chamber after isolation.

After the helium gas was removed, the chamber was again isolated from the diffusion pump, and the gas to be studied was let into the chamber. The adsorption parameters for each gas were determined from the resulting variations in chamber pressure.

The same procedure was used in the 16-in. cell up to the point of achieving cold charcoal at a low pressure. At this point, the 6-in. gate valve was closed, and the main chamber was loaded to a pre-determined pressure level with nitrogen gas. Then, the 6-in. valve was quickly opened, and the pressure-time curves for both chambers were recorded. Two types of experiments were conducted in this system. In the first type of experiment, the loading pressure of the main chamber was increased to successively higher levels before each run. The system equilibrium pressure at the conclusion of each run was returned to the pre-run value by removing gas adsorbed by the charcoal. Originally, this was accomplished by warming the system to room temperature and pumping out the desorbed gas, but it was found that the adsorbed gas could be removed by valving in the oil diffusion pump while the system was still cold. When the system equilibrium pressure had been returned to the pre-run value, the 6-in. valve was closed, and the main chamber loaded for the next run. The system equilibrium pressure was, of course, the elbow equilibrium pressure after closure of the 6-in. valve, and because the equilibrium pressure of a closed system containing an adsorbent is indicative of the amount of gas adsorbed, this meant that the charcoal contained the same amount of gas before each run. Hence, this procedure created the effect of sudden exposure of charcoal containing the same amount of gas adsorbed to successively higher pressures. In the second type of experiment, the loading pressure before each run was maintained constant for the series of runs, but the equilibrium pressure at the conclusion of a run was increased by flowing in large quantities of nitrogen gas before the next run. Thus, the second type of experiment gave the effect of sudden exposure of the same pressure to charcoal containing successively greater amounts of gas adsorbed.

3.2 CHARCOAL CONDITIONING

The types of charcoal used in this study were Columbia activated 1/8-in. charcoal pellets and National Carbon activated carbon coating mix, which were purchased in their activated state. Reactivation of the charcoal was found to be necessary both to increase the rate of adsorption of the charcoal and to render reproducible results. The procedure of reactivation depended on the type of gas adsorbed. Such gases as oxygen, water vapor, air, and hydrogen required a bake-out in vacuo at about 100°C. Also, it was found that a nitrogen purge of the charcoal

at 77°K was some aid in removing these gases. Argon and nitrogen were found to be quite easy to remove from the charcoal, requiring only exposure of the charcoal to diffusion pump action. The ease with which nitrogen is desorbed from charcoal was reported by Lazarev and Fedorova (Ref. 3), and was found to be a valuable tool to this study -- nitrogen adsorption runs could be repeated by exposing the charcoal to a diffusion pump while maintaining a cold temperature.

3.3 TEMPERATURE CONTROL

It was found that the only way a constant temperature could be maintained during an adsorption run was to completely envelope the charcoal bed with liquid nitrogen surfaces. This is because heat conduction across the charcoal-charcoal holder interface and through the low pressure residual gas is comparable to radiation from small warm surfaces. In the case of a changing pressure, the presence of a warm surface is even more severe because the degree of heat conduction is pressure dependent. A pressure dependent balance does not exist in the case of complete envelopment by coolant temperature. Figure 3 is an example of the degree of temperature control achieved in the charcoal bed during a continuous adsorption run.

3.4 TEMPERATURE MEASUREMENT

In computing pumping speeds, it is necessary to know the gas temperature, which becomes increasingly difficult to define as higher vacuums are achieved. A large measure of success has been obtained in this study by the application of the following two theorems:

1. Gas in the free-molecule region will quickly assume an average temperature determined by its enveloping temperature.
2. In cases where the enveloping surfaces have different temperatures, the average temperature can be determined by statistical weighting of the separate temperatures with the surface area of each temperature.

The first theorem is predicated on the bases that such must be the case for thermal transpiration to exist. The second theorem leads to the expression,

$$T^* = \frac{\sum_i A_i T_i}{\sum_i A_i} \quad (1)$$

where T^* is the average temperature of the gas in the region enveloped by areas A_i , each at temperature T_i .

An example of the application of Eq. (1) is given in Fig. 4, where the pressure-time response of the 16-in. main chamber is shown. In this case, the main chamber is isolated from the elbow chamber and the diffusion pump. The chamber is loaded with nitrogen gas to a pressure of 5.1×10^{-4} torr while the elbow pressure (not shown) is maintained in the low 10^{-6} -torr region. The gas in the main chamber is initially at 290°K, and the elbow pot is at 77°K. The ratio of the main chamber volume to the main chamber plus elbow volume is 0.9. Hence, with no temperature correction, the pressure in the main chamber should drop to 0.9 of its loaded value (no charcoal in the elbow and the elbow pressure neglected) when the 6-in. gate valve between the two chambers is opened. Now, using Eq. (1) to compute the characteristic temperature of the total system gives a characteristic temperature of 235°K. When this change in temperature is considered with the change in volume, a drop in main chamber pressure to 0.735 of its initial value is obtained. This corresponds to a pressure of 3.74×10^{-4} torr, which is the experimental value obtained in Fig. 4 after the 6-in. gate was opened.

4.0 RESULTS

4.1 16-IN. CELL

An example of elbow chamber pressure response when the 6-in. gate valve was opened is shown in Fig. 5. As discussed, this procedure had the effect of suddenly exposing charcoal to a high pressure. The pressure-time curve in Fig. 5, then, represents charcoal pumpdown from this high pressure. The recorder was not capable of responding fast enough to monitor the initial pressure (after expansion and cooling) to which the charcoal was exposed. A duration of 0.5 to 0.75 sec was required for the recorder to give the correct pressure response, but this presented no problem because the initial pressure could be calculated from Eq. (1) and knowledge of the separate chamber volumes and pressures before the 6-in. valve was opened.

A series of these curves corresponding to the first type of experiments in the 16-in. cell is shown in Fig. 6. In each case, the elbow pressure was the same before the 6-in. valve was opened. This means that in each case, the volume of gas adsorbed by the charcoal before its exposure to the higher pressure was the same. The different equilibrium

pressures after adsorption resulted from the adsorption of different volumes of gas after the 6-in. valve was opened. It should be mentioned that the curves shown in Fig. 6 are only representative of the actual data and were plotted by starting with the first point easily transferable to graph paper and separating successive curves by an arbitrary 5 sec for comparison. The complete data curve for each curve of Fig. 6 is similar to the curve shown in Fig. 5. The zero time mark for each of these curves is from 0.5 to 0.75 sec back of the first point shown, and in some cases the maximum point of the actual data is slightly higher than the first point shown. All calculations were made directly on the recorder chart by sliding the time scale such that zero time corresponded to the opening of the 6-in. valve.

A linear approximation of the pressure-time curves was used for the first 5 sec of each curve. The slope of the first 5 sec was measured from this approximation and plotted against the initial pressure of each curve in Fig. 7. This was repeated for the first second with no change in the results. The result of this measurement, as can be seen in Fig. 7, is that the initial slope is directly proportional to pressure. This means that the volumetric rate (at chamber conditions) at which charcoal removes gas from a system is independent of pressure provided the volume of gas adsorbed is constant. This is demonstrated in Fig. 8, and the meaning of this result will be discussed in Section 5.3.

As discussed in Section 3.1, the second series of experiments was performed in a similar manner except that the loading pressure was maintained constant while the volume of gas adsorbed by the charcoal was purposely increased between experiments. A sample collection of these curves is shown in Fig. 9. The calculated initial pressure of each of these curves is 4.55×10^{-4} torr. Again, Fig. 9 is only representative of the actual data curves which were similar to the curve shown in Fig. 5 and which revealed a slight error in the critical region near zero time after they were transferred to graph paper.

An analysis was performed on this series of curves identical to the analysis for the first series. The resulting initial exhaust rate is plotted against volume of gas adsorbed in Fig. 10.

4.2 RESULTS-COLD WALL CELL

Experiments similar to those reported earlier (Ref. 1) were performed in the cold wall cell except that charcoal paste was used instead

of the charcoal pellets reported in Ref. 1. In addition, other gases besides nitrogen were examined. The results of the data from this system and the experiments reported earlier (Ref. 1) are tabulated in Table 1.

5.0 ANALYSIS

5.1 SYNOPSIS OF EARLIER ANALYSIS

It has been shown in an earlier report (Ref. 1) that the residual gas pressure, P , of a chamber in which a metered throughput of nitrogen gas is pumped by charcoal can be expressed by:

$$P = \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a t + \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{\alpha A \sqrt{\frac{R T_c}{2\pi M}}} \quad (2)$$

where A is the projected surface area of the charcoal, P_a is the atmosphere pressure, T_a is the atmosphere temperature, T_c is the chamber gas temperature, R is the universal gas constant, M is the molecular mass, and $\left(\frac{dv}{dt} \right)_a$ is the constant volumetric rate at which gas enters the chamber in units of atm cc/sec. The three constants, α , ζ , and k , are fundamental adsorption constants which are referred to as adsorption parameters. The constant α is defined as the ratio of the rate at which molecules adhere to a surface to the rate at which they strike the surface. The constant ζ is defined from Henry's adsorption isotherm (Ref. 4) by

$$P_\infty = \frac{\zeta}{A} V_{ad} \quad (3)$$

where P_∞ is the equilibrium pressure resulting after adsorption of a volume of gas (referenced to standard atmospheric pressure and 293°K), V_{ad} . Neglecting the slight amount of gas not adsorbed, the amount of gas adsorbed, V_{ad} , is determined by

$$V_{ad} = \left(\frac{dv}{dt} \right)_a t \quad (4)$$

In Ref. 1, the constant ζ/A was represented by γ . The constant k expresses the relation between residual gas pressure, P , and equilibrium pressure, P_∞ , by

$$P - P_\infty = k P + C \quad (5)$$

where C is a flow rate dependent term defined by

$$C = (1 - k) \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{\alpha A \sqrt{\frac{R T_c}{2 \pi M}}} \quad (6)$$

It should be noted that in Eq. (2) there is not a description of the transient region, i. e., the region of the pressure-time curve between onset of pressure rise caused by gas flow into the chamber and establishment of a linear pressure rise.

5.2 COMPENDIUM OF THIS ANALYSIS

The exhaust rate, adsorption rate, and desorption rate will be derived along conventional lines from definitions and the relations of Section 5.1. In particular, the exhaust rate will be derived from the definition of exhaust rate and Eq. (2). The adsorption rate (gross rate of gas removal of an adsorption bed) will be derived from analogy to the gross rate of gas removal by a conventional pump (pumping speed). The adsorption rate and exhaust rate will, in turn, determine the desorption rate. However, the relations of Section 5.1 which are a priori to this analysis do not include any description of the transient portion of the pressure-time relation. Therefore, it would be expected that the derived rates would be unmeaningful for transient pressures, and this is shown to be the case.

In Section 5.6, the derived expressions for exhaust rate and desorption rate will be corrected by imposing constraints on the behavior of the adsorption rate. It will be shown that the corrected versions of exhaust rate and desorption rate agree with experimental data even in the transient region.

Thus, the analytical support for the primary goal of this analysis is set. Where the original exhaust rate was derived from Eq. (2), the corrected form of exhaust rate is used to correct Eq. (2). This correction is shown to give an expression (in differential form) which not only contains Eq. (2) but also has meaning for the transient region.

In Section 5.8, the validity of neglecting the amount of gas remaining in the chamber after a period of adsorption relative to the amount of gas which is adsorbed will be established.

5.3 EXHAUST RATE

Exhaust rate is defined as the volumetric rate of gas removal at chamber conditions. Let E denote the exhaust rate; then, by definition,

$$E = \left(\frac{dv}{dt} \right)_E = \frac{V_c}{P} \left(\frac{dP}{dt} \right)_E \quad (7)$$

where $\left(\frac{dP}{dt} \right)_E$ is the rate of pressure change attributable to gas removal and V_c is the chamber volume.

In the case of a gas pressure change resulting from exhausting under the condition of a continuous inleakage, conservation of mass requires that

$$\left(\frac{dP}{dt} \right)_R = \left(\frac{dP}{dt} \right)_{\text{inleakage}} - \left(\frac{dP}{dt} \right)_E \quad (8)$$

where $\left(\frac{dP}{dt} \right)_R$ is the rate of change of residual gas pressure and $\left(\frac{dP}{dt} \right)_{\text{inleakage}}$ is the rate of pressure rise that would exist if there were no gas removal. It can be shown that

$$\left(\frac{dP}{dt} \right)_{\text{inleakage}} = \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{V_c} \quad (9)$$

and on recalling that Eq. (2) gives the time dependence of residual pressure,

$$\left(\frac{dP}{dt} \right)_R = \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a \quad (10)$$

Therefore,

$$\left(\frac{dP}{dt} \right)_E = \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{V_c} - \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a \quad (11)$$

or

$$E = \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{P} - \frac{\zeta V_c \left(\frac{dv}{dt} \right)_a}{A(1-k)P} \quad (12)$$

Equation (12) gives E as an inverse function of P . However, during continuous adsorption, P is a function of V_{ad} , and it was shown experimentally in Section 4.1 and Fig. 8 that for a constant V_{ad} , E is independent of P . Hence, E should more correctly be expressed as a function of V_{ad} . That is (by inserting $P = \frac{\gamma}{1-k} V_{ad} + \frac{C}{1-k}$ - Eq. (6), Ref. 1),

$$E = \frac{(1 - k) A P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a} - \zeta V_c \left(\frac{dv}{dt} \right)_a}{\zeta V_{ad} + C A} \quad (13)$$

A direct experimental verification of Eq. (13) requires measurement of E for increments in V_{ad} with an initial P_i (see Fig. 15) such that $(P_i - P_\infty)$ remains constant (Ref. 2). Such an experimental condition is difficult to achieve, but the variation of the behavior of E for increments in V_{ad} all at the same initial P_i was accomplished by the second series of experiments discussed in Section 4.1. A uniform decrease in E was found to be the result, as is shown in Fig. 10.

In plotting the variation of E , it was found to be more expedient to deal with Eq. (12) rather than Eq. (13), and this practice of using the parameter P instead of V_{ad} will be continued for the remainder of this analysis. However, it must be remembered that Eq. (12) is a parametric equation and that the variation of E is actually controlled by V_{ad} .

5.4 ADSORPTION RATE

When a constant throughput is admitted to a vacuum chamber which is being initially maintained at its base pressure, P_s , by a conventional pump, the chamber pressure rises to equilibrium pressure. It can be shown (Ref. 5) that at the equilibrium pressure, P ,

$$Q = E P = S^* (P - P_s) = S^* \Delta P \quad (14)$$

where E is the exhaust rate, S^* is the pumping speed for a conventional pump, and P is the increment in pressure resulting from the introduction of Q , and Q is the throughput defined by

$$Q = P \left(\frac{dv}{dt} \right) = P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a} \quad (15)$$

Taking the adsorption rate to be the pumping speed of an adsorption pump, an expression relating the exhaust rate to adsorption rate can be obtained similar to Eq. (14) with the notable distinction that no longer is an equilibrium condition being described. This is because some fraction of Q is always left unadsorbed which causes the chamber pressure to rise.

Let δ denote the fraction of Q which is not adsorbed. The adsorption expression analogous to Eq. (14) is

$$Q - \delta Q = E P = S (P - P_\infty) \quad (16)$$

where S is the adsorption rate, P_∞ is the base or equilibrium pressure (variable with amount of gas adsorbed), P is the instantaneous gas pressure, and E is the exhaust rate. The term $(P - P_\infty)$ is analogous to ΔP in Eq. (14).

From Eq. (16), the defining expression for the adsorption rate now becomes

$$S = \frac{Q - \delta Q}{\Delta P} \quad (17)$$

The term δQ is reflected in the residual gas pressure buildup. That is,

$$\delta Q = V_c \left(\frac{dP}{dt} \right)_R \quad (18)$$

Using the definition of Q , Eq. (5), and Eq. (18), the definition of S can now be expressed as

$$S = \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a} - V_c \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a}{kP + C} \quad (19)$$

5.5 DESORPTION RATE AND VARIATIONS OF RATES

Both E and S stem from analytical descriptions of two fundamental volumetric rate processes. The adsorption rate, S , describes the gross volumetric rate of gas removal, whereas the exhaust rate, E , describes the actual (net) volumetric rate of gas removal. Any difference between these two rates must be attributable to gas that is returned to the chamber, i. e., desorption. Let D denote the volumetric rate of desorption. Then,

$$D = S - E \quad (20)$$

In order to simplify, let Q_{ad} denote $P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a} - V_c \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a$.

The collected expressions for E , S , and D now become

$$\begin{aligned} E &= \frac{Q_{ad}}{P} \\ S &= \frac{Q_{ad}}{kP + C} \\ D &= \frac{Q_{ad}}{kP + C} - \frac{Q_{ad}}{P} \end{aligned} \quad (21)$$

For purposes of measurement and calculation, the difference between Q and Q_{ad} is negligible for the cases considered here.

The variations of E , S , and D through a continuous adsorption run are shown in Fig. 11. The values of k , C , and Q_{ad} are taken from run No. 5 reported in Ref. 1. Again it is emphasized that these are parametric equations and that the controlling parameter is V_{ad} . The

conversion from a functional dependence on P to a functional dependence on V_{ad} can always be accomplished with Eq. (2).

The behavior of E , S , and D demonstrated in Fig. 11 seem reasonable except at the low pressure (low volume of gas adsorbed) end. This is because Eq. (2) does not include the transient region. That is, the equations identified as Eq. (21) were derived from an expression which does not apply for

$$P < \frac{Q}{a A \sqrt{\frac{R T_c}{2 \pi M}}} \quad (22)$$

Hence, it is not surprising to find an anomalous behavior in this region.

5.6 CONSTRAINTS ON ADSORPTION RATE

The anomalous behavior for E , S , and D can be removed by considering the influence of two constraints on S in the analytical description of E and D . The first constraint is that S remain constant when the flow is terminated and the dynamic pressure decays to an equilibrium pressure. This constraint was experimentally verified in an earlier report (Ref. 2) and agrees with the concept presented here that S is controlled by the total volume of gas adsorbed which changes negligibly during a pressure decay to equilibrium. The second constraint is that S be equal to D at equilibrium.

The influence of these two constraints on E and D can be seen by considering (see Fig. 15) a specific instantaneous pressure, P_1 , and its corresponding equilibrium pressure, P_{∞_1} . By Eq. (21), S at $P = P_1$ is given by:

$$S|_{P=P_1} = \frac{Q_{ad}}{k P_1 + C} \quad (23)$$

From Eq. (5), P_1 and P_{∞_1} are related by

$$P_1 - P_{\infty_1} = k P_1 + C \quad (24)$$

Now, solving Eq. (24) for P_1 gives

$$P_1 = \frac{P_{\infty_1} + C}{1 - k} \quad (25)$$

Thus,

$$P_1 - P_{\infty_1} = \frac{k P_{\infty_1} + C}{1 - k} \quad (26)$$

and therefore,

$$k P_1 + C = \frac{k P_{\infty_1} + C}{1 - k} \quad (27)$$

Hence,

$$S|_{P=P_1} = (1 - k) \frac{Q_{ad}}{k P_{\infty_1} + C} \quad (28)$$

But, $\frac{Q_{ad}}{k P_{\infty_1} + C}$ is just the value of S at a dynamic pressure corresponding to the value of P_{∞_1} . Therefore,

$$S|_{P=P_1} = (1 - k) S|_{P=P_{\infty_1}} \quad (29)$$

Now, applying the result of both the above constraints on S , the value of S at $P = P_1$ must be the same as the value of D at $P = P_{\infty_1}$.

That is,

$$S|_{P=P_1} = D|_{P=P_{\infty_1}} \quad (30)$$

Therefore, from Eqs. (30) and (29)

$$(1 - k) S|_{P=P_{\infty_1}} = D|_{P=P_{\infty_1}} \quad (31)$$

Equation (31) must be true for any specific pressure. Hence, in general,

$$D = (1 - k) S \quad (32)$$

And, using Eq. (20), the relation between E and S becomes

$$E = k S \quad (33)$$

Thus, the collection of expressions for E , S , and D now becomes

$$\begin{aligned} S &= \frac{Q_{ad}}{k P + C} \\ D &= (1 - k) \frac{Q_{ad}}{k P + C} \\ E &= \frac{Q_{ad}}{P + \frac{C}{k}} \end{aligned} \quad (34)$$

A plot of the equations identified as Eq. (34) (using the same parameters as for Fig. 11) is shown in Fig. 12. Not only is the anomalous behavior of Fig. 11 removed in Fig. 12 but the increment in pressure between the S and D curve corresponds very well with the drop in pressure that is measured when the flow is terminated. This is demonstrated in Fig. 13 where a discontinuous pressure-time curve (run No. 5, Ref. 1) from the 6-in. cell is shown with the S , D , and E curves. The first decay of the pressure-time curve goes from 1.5×10^{-5} to 0.4×10^{-5} torr for a ΔP of 1.1×10^{-5} torr. Locating the 1.5×10^{-5} -torr point on the S curve, then the corresponding D value is at 0.35×10^{-5} torr for a ΔP of 1.15×10^{-5} torr. The other values of ΔP are shown.

The variation of E during a discontinuous run is shown in Fig. 14 where E is considered to obey Eq. (15) during the transition region. The values of E at which the transient curves intercept the continuous run E curve is in good agreement with the values of E at the conclusion of each transition as determined by dropping vertical lines from the ΔP lines of Fig. 13. To avoid confusion, just the ends of the ΔP lines are shown.

5.7 PRESSURE-TIME RELATION AND TRANSIENT REGION

It was shown in Section 5.5 that the analytical formulation of E, S, and D generated the anomalous condition of a value of E larger than the value of S for pressures in the transient region. It was explained there that this anomalous behavior was a result of deriving the expression of E from Eq. (2) which has no meaning for pressures in the transient region. In Section 5.6, a corrected expression for E was obtained by imposing reasonable constraints on the behavior of S. The corrected form of E, then, gave a corrected form of D, and it was shown that the pressure increment between S and the corrected form of D was in good agreement with pressure increments determined experimentally.

The difference between the value of E derived from Eq. (2) and expressed in Eq. (21) and the corrected form of E expressed in Eq. (34) is very slight -- amounting to only the C/k term which is negligible relative to P for pressures greater than transient pressures. However, this slight correction of E produces a behavior for E which agrees with experimental data and extends into the transient region. Thus, if the corrected version of E is inserted in the mass balance equation (Eq. (8)), a differential equation for the residual gas pressure should result which contains not only Eq. (2) but the transient region as well.

The validity of this is easy enough to test. If

$$E = \frac{Q_{ad}}{P + \frac{C}{k}} \quad (35)$$

then from Eq. (7),

$$\left(\frac{dP}{dt}\right)_E = \left(\frac{kP}{kP + C}\right) \frac{Q_{ad}}{V_c} \quad (36)$$

and, upon returning to Eq. (8),

$$\left(\frac{dP}{dt}\right)_R = \frac{Q}{V_c} - \left(\frac{kP}{kP + C}\right) \frac{Q_{ad}}{V_c} \quad (37)$$

or

$$\left(\frac{dP}{dt}\right)_R = \frac{Q}{V_c} - \left(\frac{kP}{kP + C}\right)(1 - \delta) \frac{Q}{V_c} \quad (38)$$

Now, for $P \approx 0$, Eq. (38) gives $\left(\frac{dP}{dt}\right)_R \approx \frac{Q}{V_c}$ which is the slope that results from no adsorption in agreement with experimentally determined pressure-time curves. As P increases until $P > \frac{C}{1-k}$,

so that $\frac{kP}{kP + C} \approx 1$, then Eq. (38) gives $\left(\frac{dP}{dt}\right)_R \approx \delta \frac{Q}{V_c}$ which is the same as the slope of Eq. (2) as expressed by Eq. (10). Thus, it appears that the slope of the residual pressure-time relation as predicted by Eq. (38) does indeed undergo the proper variation with pressure, and the integrated form of Eq. (38) should contain both Eq. (2) and the transient region.

The use of a single rate of exhaust to explain the transient region is more satisfying from a theoretical viewpoint than the three rates of exhaust reported in Ref. 2.

5.8 VOLUME OF GAS REMAINING AFTER ADSORPTION

Throughout this work, it has been assumed that the volume of gas unadsorbed was negligible and that Eq. (4) was an adequate expression for the volume of gas adsorbed. Let V_{ad}^* denote the volume of gas not adsorbed. Then

$$V_{ad} = \left(\frac{dv}{dt}\right)_a t - V_{ad}^* \quad (39)$$

and

$$V_{ad}^* = \frac{P}{P_a} \frac{T_a}{T_c} V_c \quad (40)$$

Therefore,

$$P_\infty = \frac{\zeta}{A} \left(\frac{dv}{dt}\right)_a t - \frac{\zeta}{A} \frac{P}{P_a} \frac{T_a}{T_c} V_c \quad (41)$$

Hence, Eq. (2) changes to

$$P = \frac{\zeta \left(\frac{dv}{dt}\right)_a t}{A(1-k)} - \frac{\zeta P T_a V_c}{A(1-k) P_a T_c} + \frac{C}{1-k} \quad (42)$$

or

$$P \left[1 + \frac{\zeta}{A(1-k)} \frac{V_c}{P_a} \frac{T_a}{T_c} \right] = \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt}\right)_a t + \frac{C}{1-k} \quad (43)$$

Thus, Eq. (43) reduces to Eq. (2) if $\frac{\zeta}{A(1-k)} \frac{V_c}{P_a} \frac{T_a}{T_c}$ is small relative to 1 -- say 0.1. That is, Eq. (2) is satisfied if

$$\frac{\zeta}{A(1-k)} \frac{V_c}{P_a} \frac{T_a}{T_c} < 10^{-1} \quad (44)$$

Using $T_c = 77^\circ K$ and $\zeta = 1.1 \times 10^{-3}$ torr $\text{cm}^2/\text{atm cc}$, then V_{ad}^* is negligible provided

$$\frac{V_c}{A} < 1.7 \times 10^4 \frac{\text{cc}}{\text{cm}^2} \quad (45)$$

Most research vessels have a $\frac{V_c}{A} \approx 10^3 \frac{\text{cc}}{\text{cm}^2}$, but it is conceivable that in the application of charcoal adsorption, a value of $\frac{V_c}{A}$ could be obtained which would approach or exceed $1.7 \times 10^4 \text{ cc/cm}^2$. However, it would not be difficult to include V_{ad}^* if such becomes necessary.

It is interesting to note that $\frac{\zeta}{A(1-k)} \frac{V_c}{P_a} \frac{T_a}{T_c}$ in Eq. (43) is the δ of Eq. (16). This is easy to see by inserting the definition of Q into Eqs. (12) and (16). Thus, δ is a flow rate independent term which becomes a convenient figure of merit or quality number for describing charcoal pumps. If a mass flow $\frac{dm}{dt}$ is introduced into a chamber pumped by charcoal, then residual mass will accumulate (after transition) at the rate of $\delta \left(\frac{dm}{dt} \right)$, and Eq. (34) will describe exhaust rate and adsorption rate provided $\delta < 0.1$.

6.0 CONCLUSIONS

The following conclusions can be made from this study of vacuum cryosorption by activated charcoal:

1. Charcoal cools primarily by radiation and must be completely enveloped by the temperature desired. The time required for cooling is on the order of several hours unless a helium purge is applied.
2. The behavior of charcoal adsorption can be adequately expressed by three constants: the sticking fraction, α ; the constant of proportionality between equilibrium pressure and specific volume of gas adsorbed, ζ ; and the constant of proportionality between instantaneous pressure and equilibrium pressure, k .
3. The exhaust rate during adsorption of a continuous inflow is related to adsorption rate by

$$E = kS$$

and the adsorption rate is expressed by

$$S = \frac{(1 - \delta) Q}{\Delta P}$$

Both adsorption rate and exhaust rate are pressure independent but inversely dependent on the volume of gas adsorbed.

4. The expression

$$P = \frac{\zeta}{A(1-k)} \left(\frac{dv}{dt} \right)_a t + \frac{P_a \left(\frac{dv}{dt} \right)_a \frac{T_c}{T_a}}{\alpha A \sqrt{\frac{RT_c}{2\pi M}}}$$

describes the pressure-time relation resulting from continuous adsorption after transient to a steady pressure rise. It does not account for the transient region. A more complete description of the pressure-time relation is given by the differential equation

$$\frac{dP}{dt} = \frac{Q}{V_c} - \left(\frac{kP}{kP+C} \right) (1-\delta) \frac{Q}{V_c}$$

5. The fraction of gas admitted to an adsorption bed that is not adsorbed, δ , is constant, and the amount of gas not adsorbed has negligible influence on the analytical expressions produced here provided that

$$\delta < 10^{-1}$$

or

$$\frac{V_c}{A} < 10^4 \frac{cc}{cm^2}$$

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TABLE 1
RESULTS OF COLD WALL CELL

Absorbate	Nitrogen	Oxygen	Argon	Hydrogen	Helium	Nitrogen	Hydrogen
Temperature	77°K	77°K	77°K	77°K	77°K	77°K	77°K
Adsorbent	Charcoal Paste	Charcoal Paste	Charcoal Paste	Charcoal Paste	Charcoal Paste	Charcoal Pellets	Charcoal Pellets
Pumping Speed, ℓ/sec	15.1	14.9	7.83	0.4	0	270	0
Specific Pumping Speed, ℓ/sec cm ²	4.8 x 10 ⁻²	4.75 x 10 ⁻²	2.49 x 10 ⁻²	1.3 x 10 ⁻³	0	0.86	0
Specific Rate of Strike, ℓ/sec cm ²	6.15	5.65	5.15	23	16.2	6.15	23
Specific Exhaust Rate, ℓ/sec cm ²	2.3 x 10 ⁻²	2.42 x 10 ⁻²	1.03 x 10 ⁻²	-	0	0.54	0
Sticking Fraction, α	7.8 x 10 ⁻³	8.42 x 10 ⁻³	4.85 x 10 ⁻³	5.6 x 10 ⁻⁵	0	0.14	0
Adsorption Constant, k	0.48	0.51	0.41	-	0	0.625	0
Isotherm Constant, ζ, $\frac{\text{torr cm}^2}{\text{atm cc}}$	13 x 10 ⁻³	9.65 x 10 ⁻³	12 x 10 ⁻³	-	0	1.1 x 10 ⁻³	0
Pressure Region Investigated, torr	10 ⁻⁸ to 10 ⁻³	10 ⁻⁶ to 10 ⁻⁴	10 ⁻⁶ to 10 ⁻⁴	10 ⁻⁵	10 ⁻⁵	10 ⁻⁸ to 10 ⁻²	10 ⁻⁵

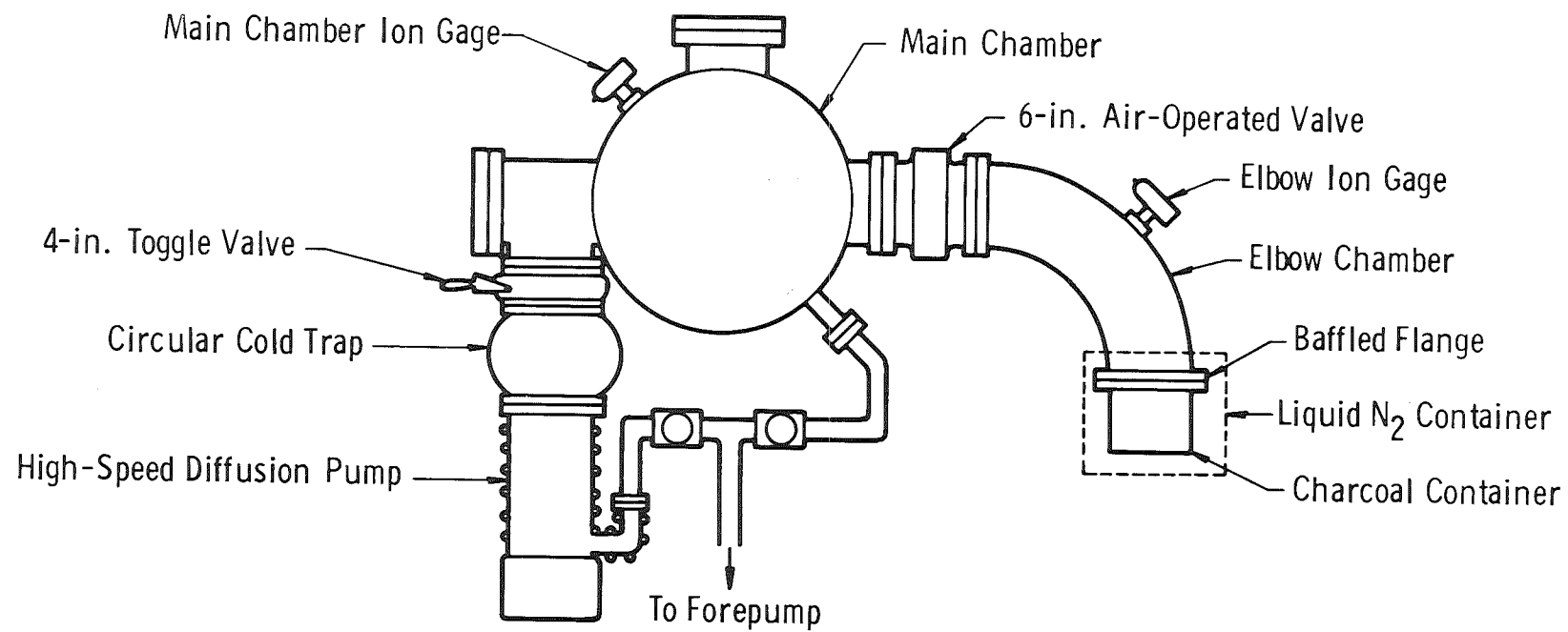


Fig. 1 Schematic of 16-in. Cell

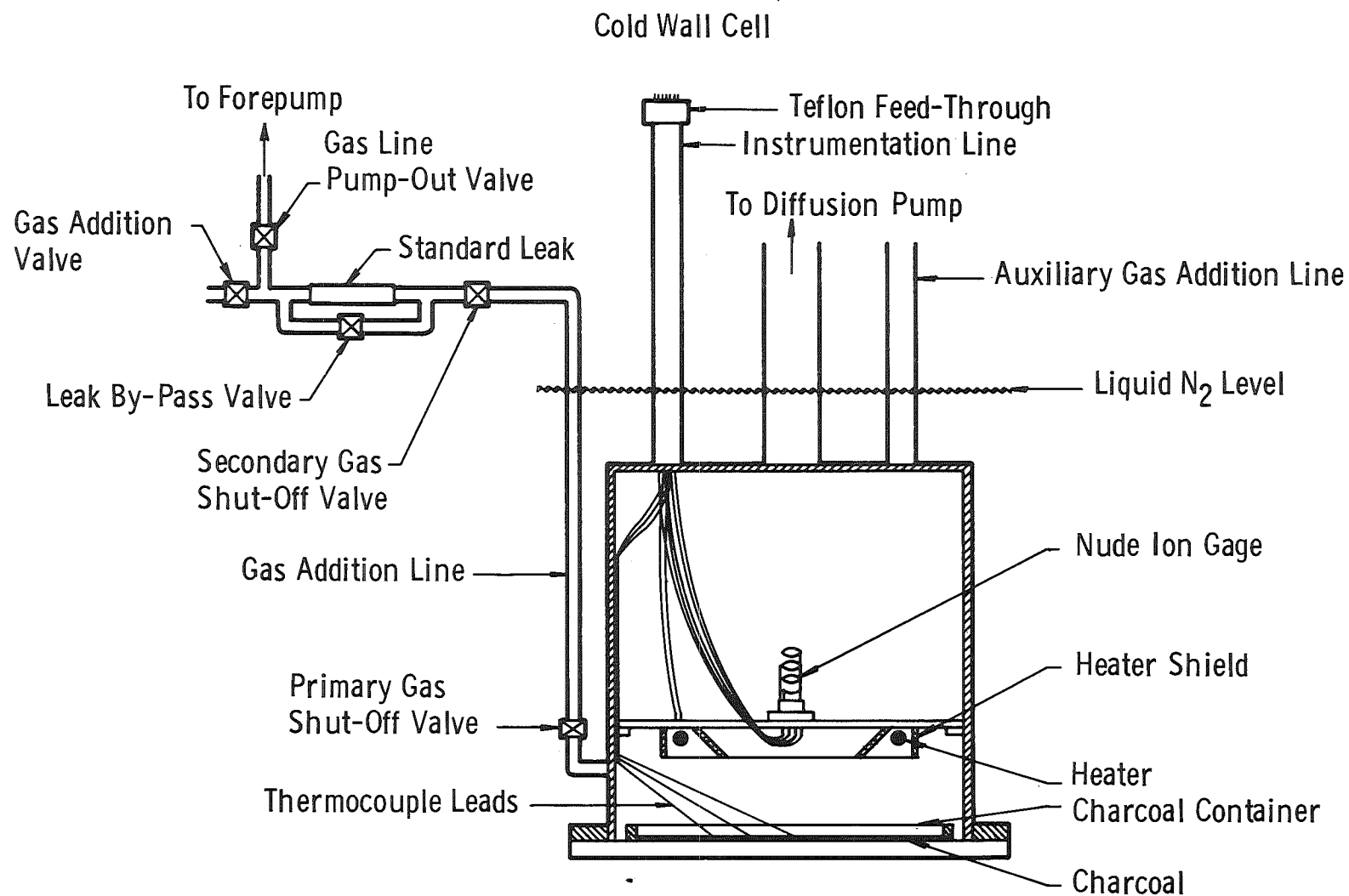


Fig. 2 Schematic of Cold Wall Cell

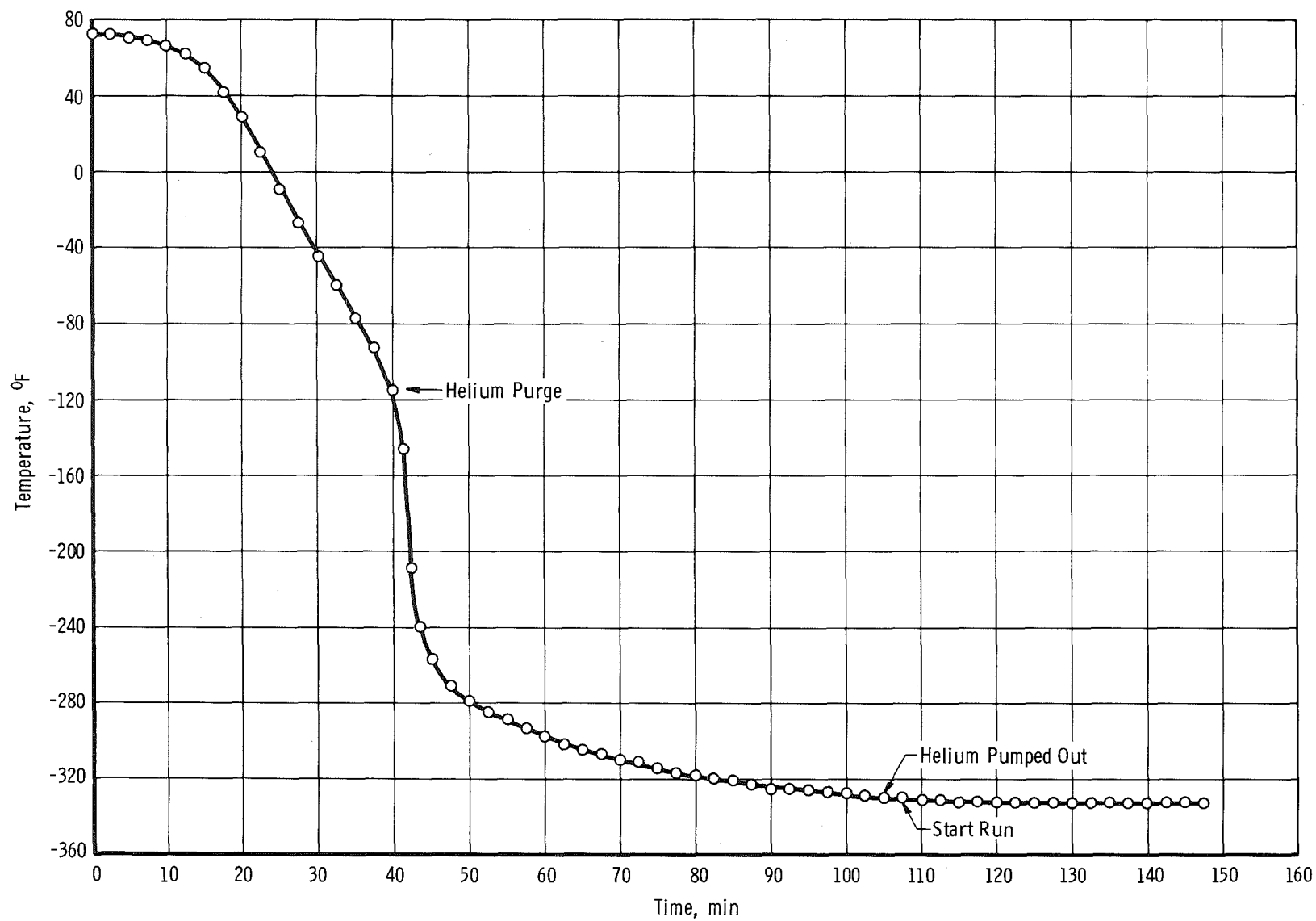


Fig. 3 Temperature Response of Cold Wall Cell

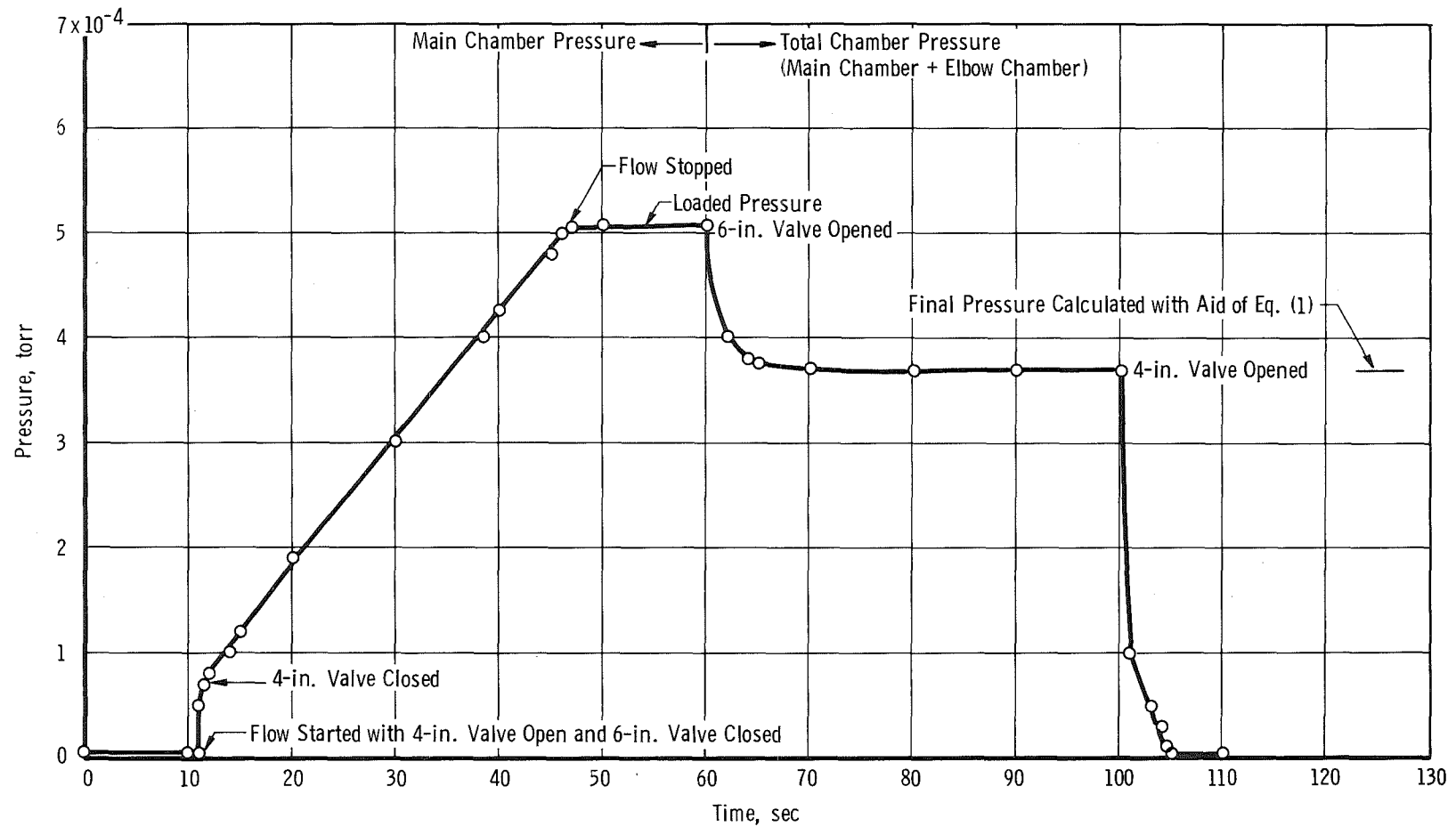


Fig. 4 16-in. Chamber Pressure Response

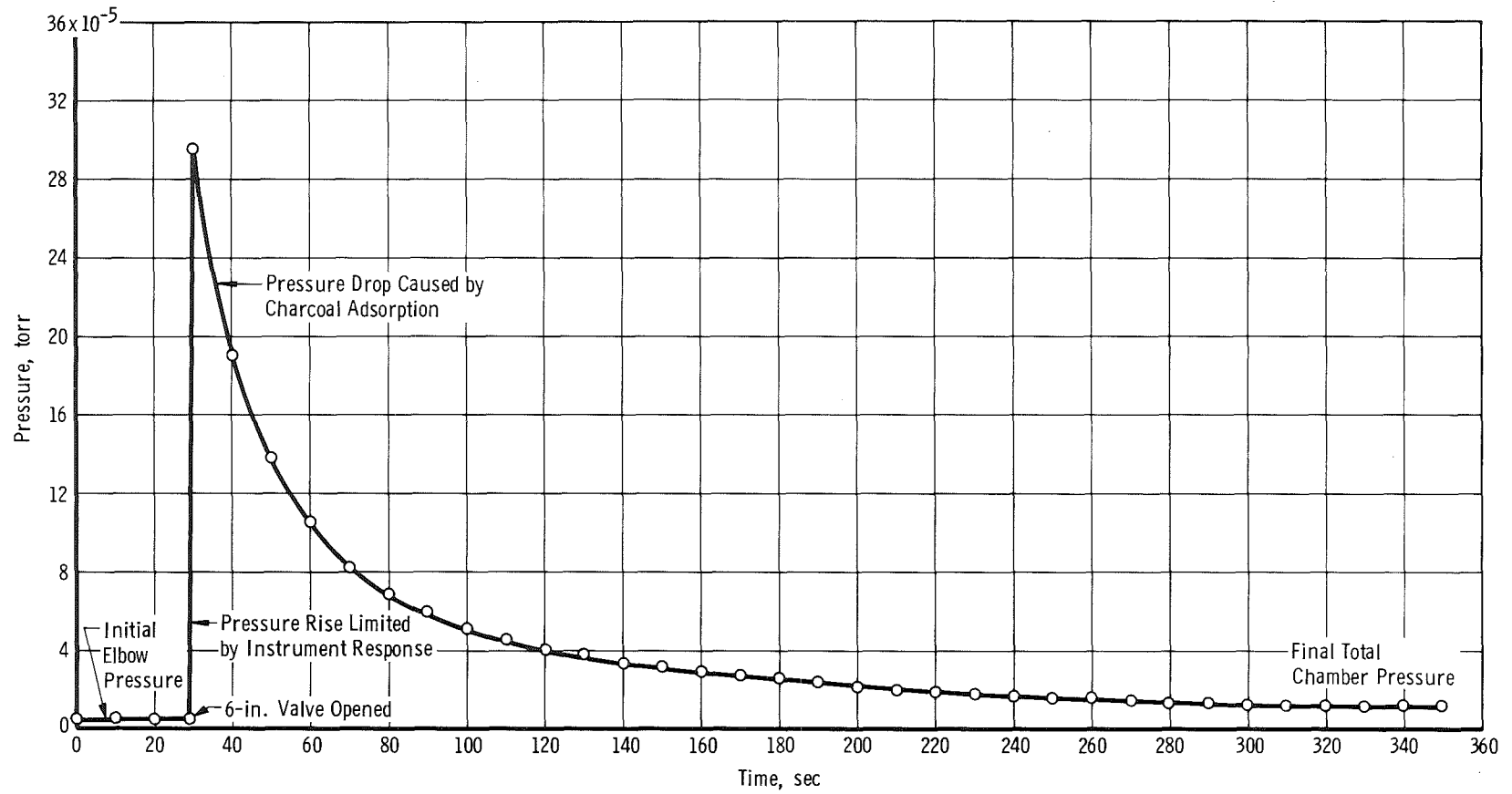


Fig. 5 Elbow Chamber Pressure Response

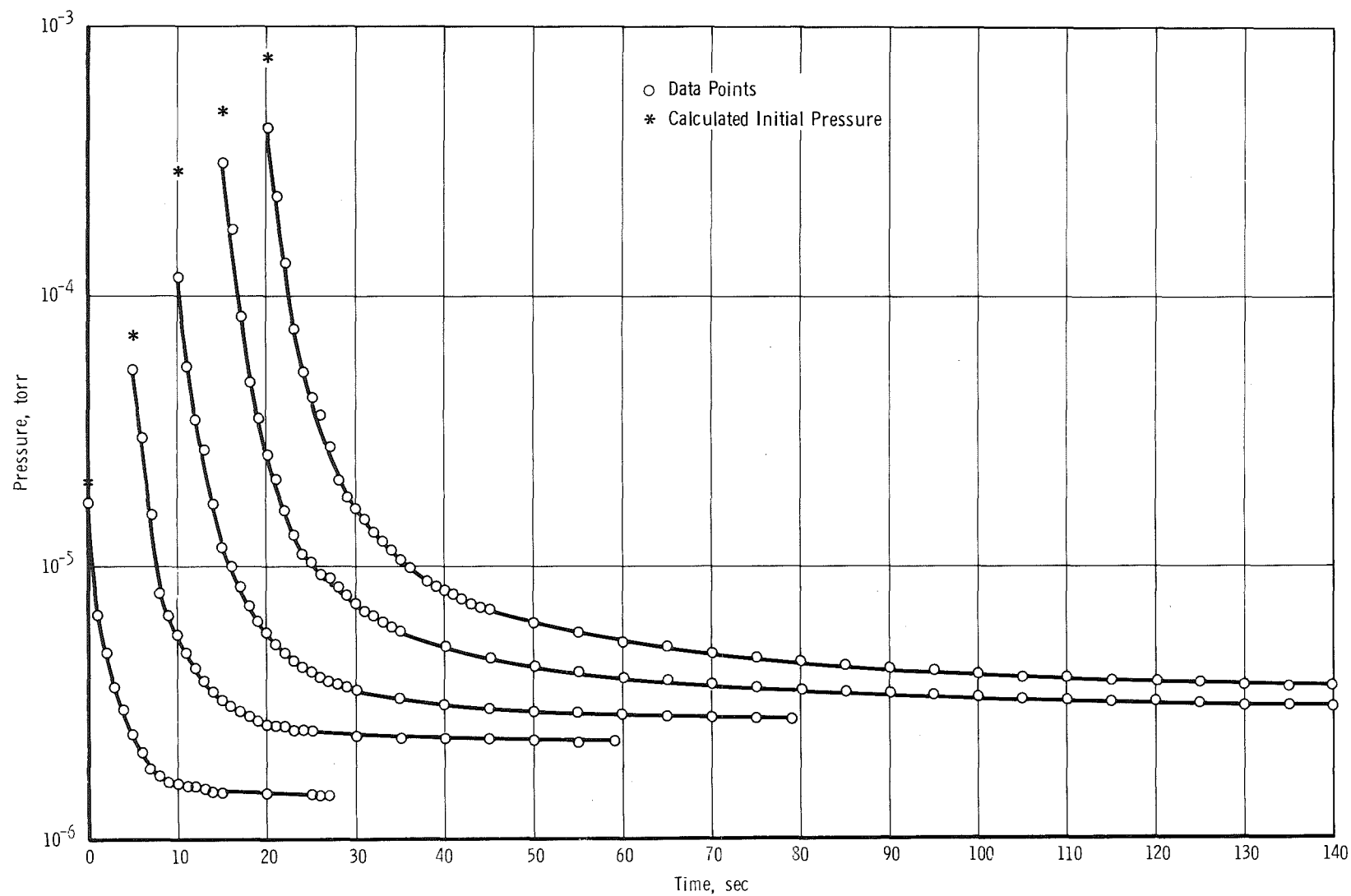


Fig. 6 Series of Pressure Drops at Constant Initial V_{ad}

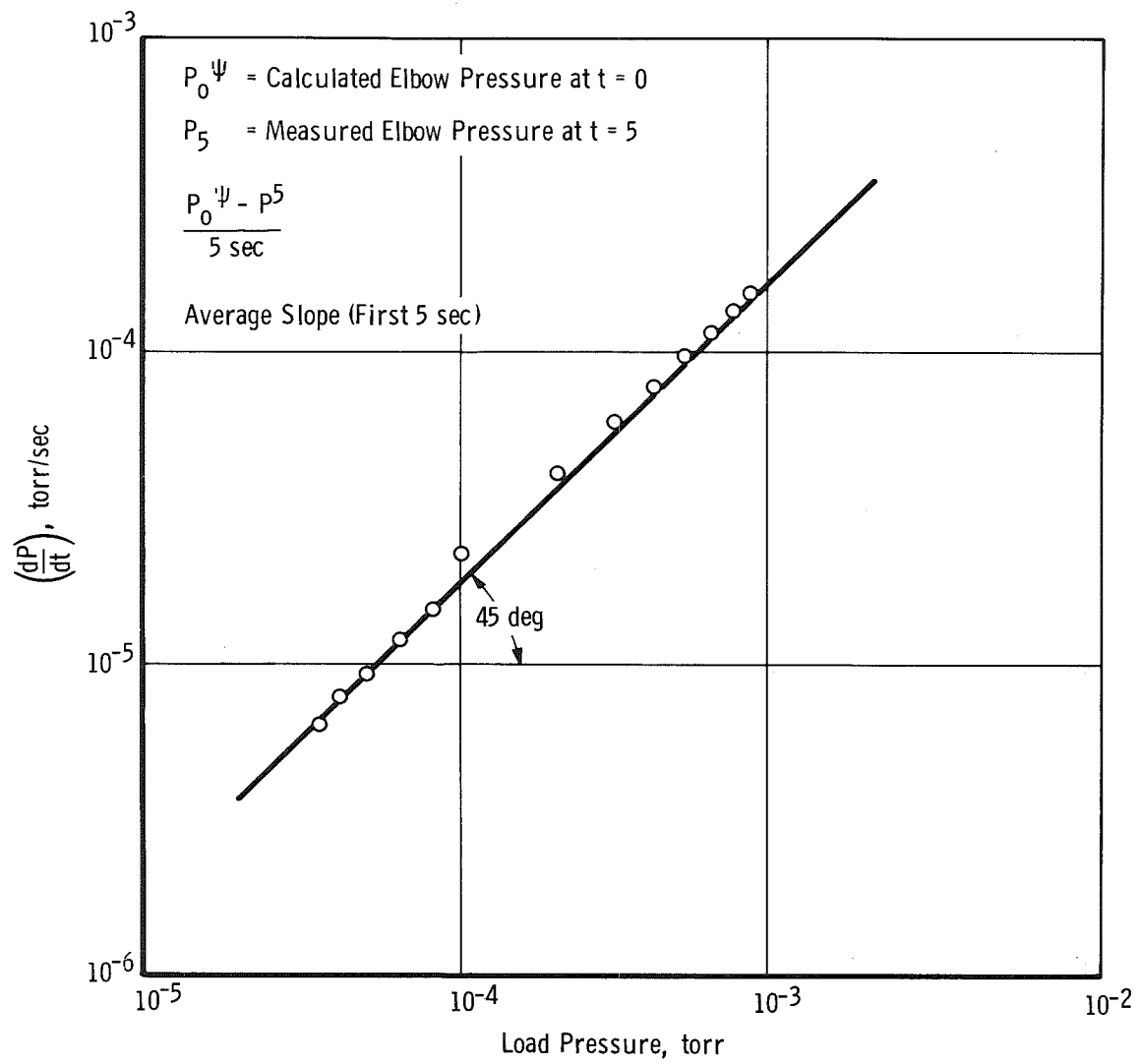


Fig. 7 Initial Slopes of Pressure Drops vs Initial Elbow Pressure

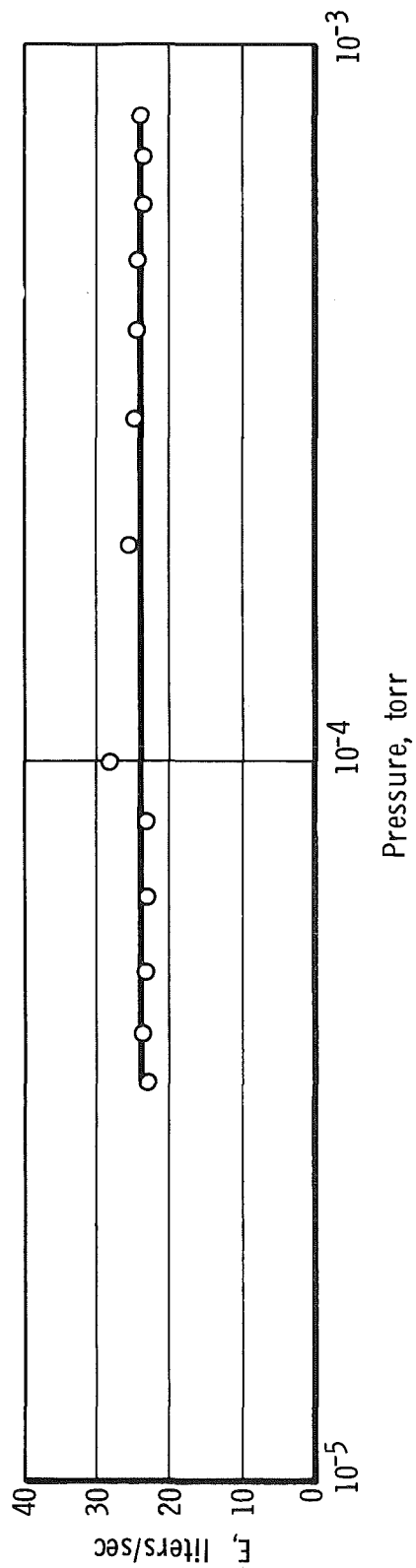


Fig. 8 Initial Volumetric Pumping Speed vs Initial Pressure

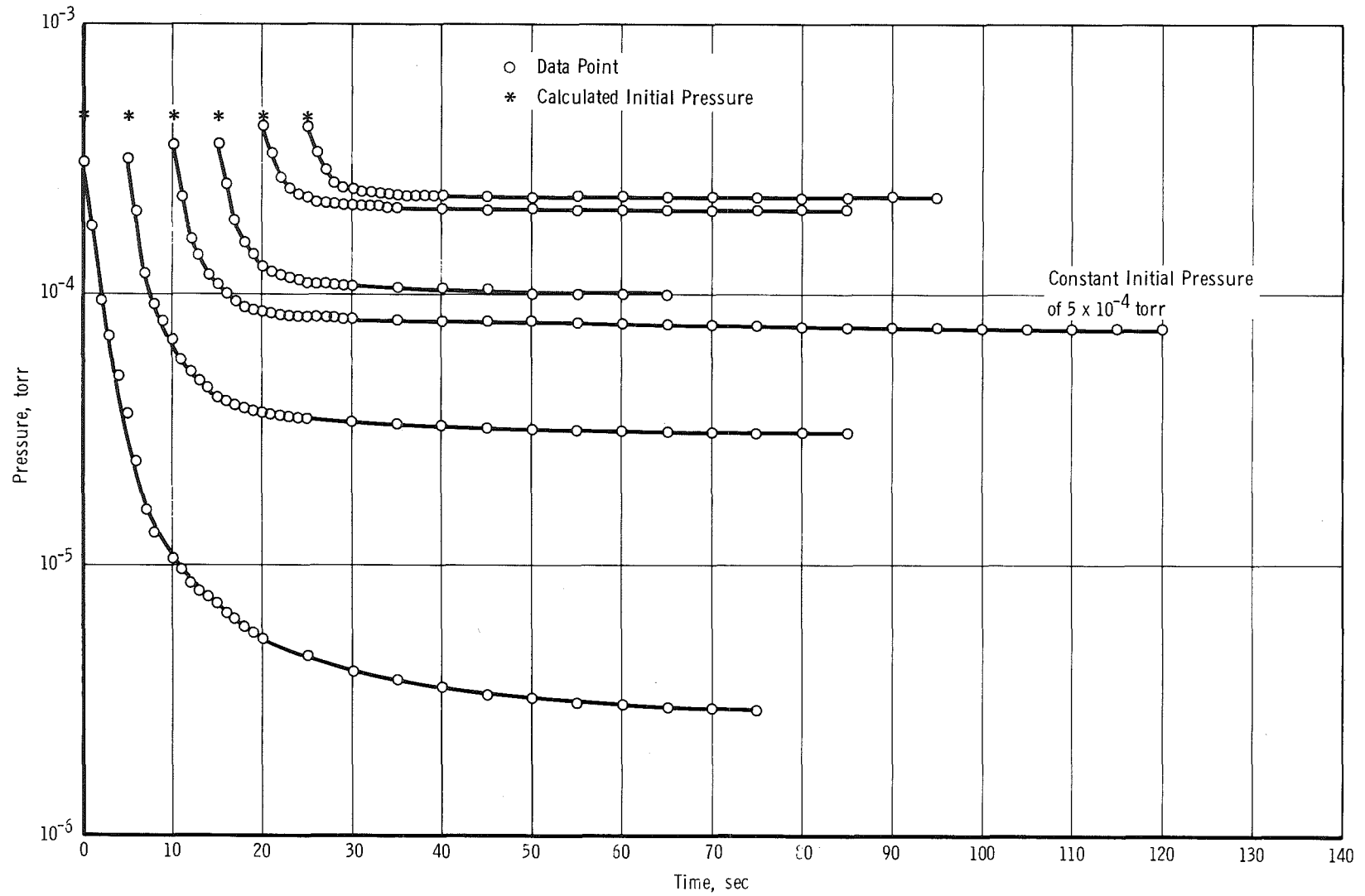


Fig. 9 Series of Pressure Drops at Constant Initial Pressure

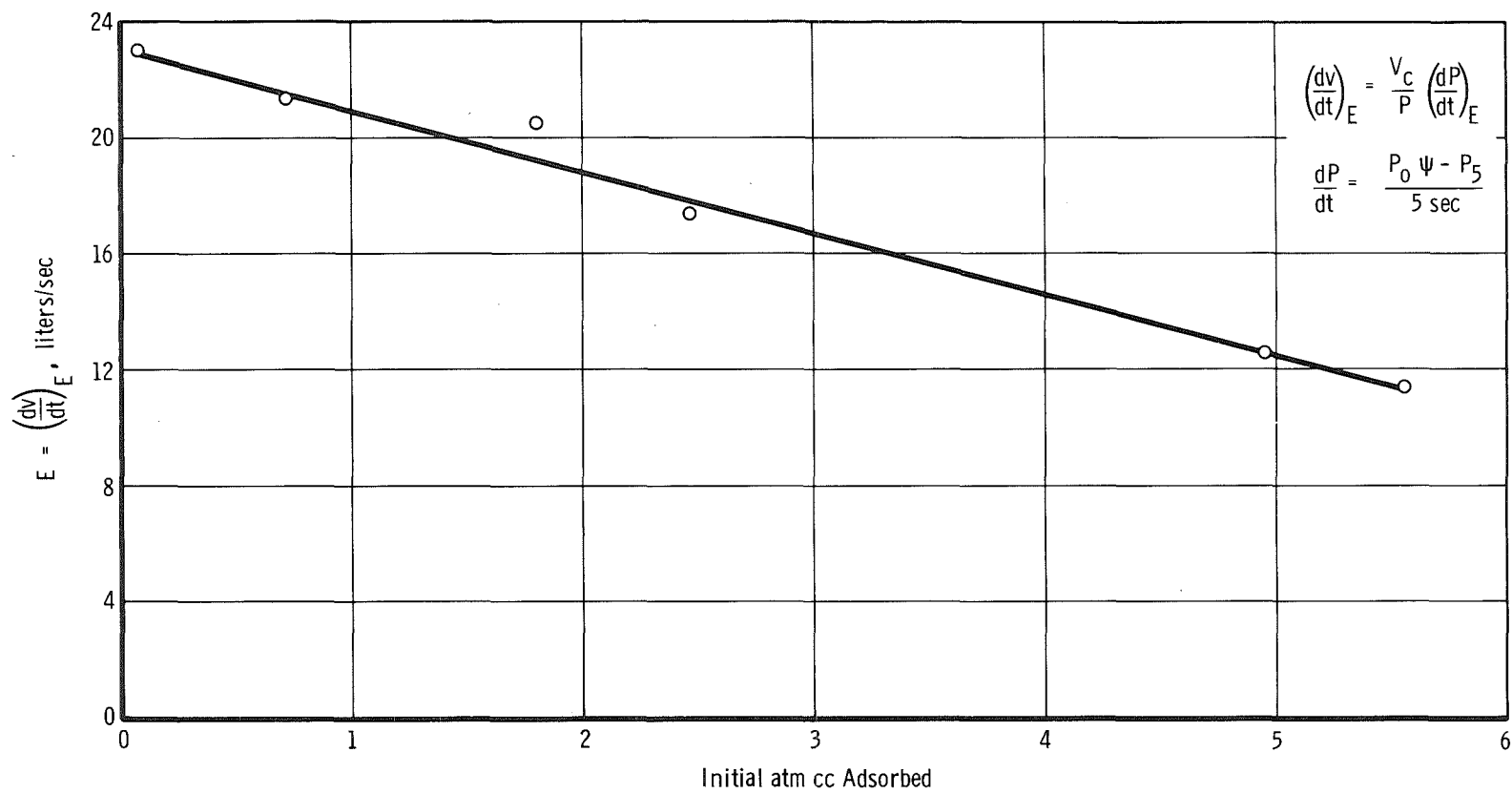


Fig. 10 Initial Volumetric Rate of Exhaust vs Initial Pressure

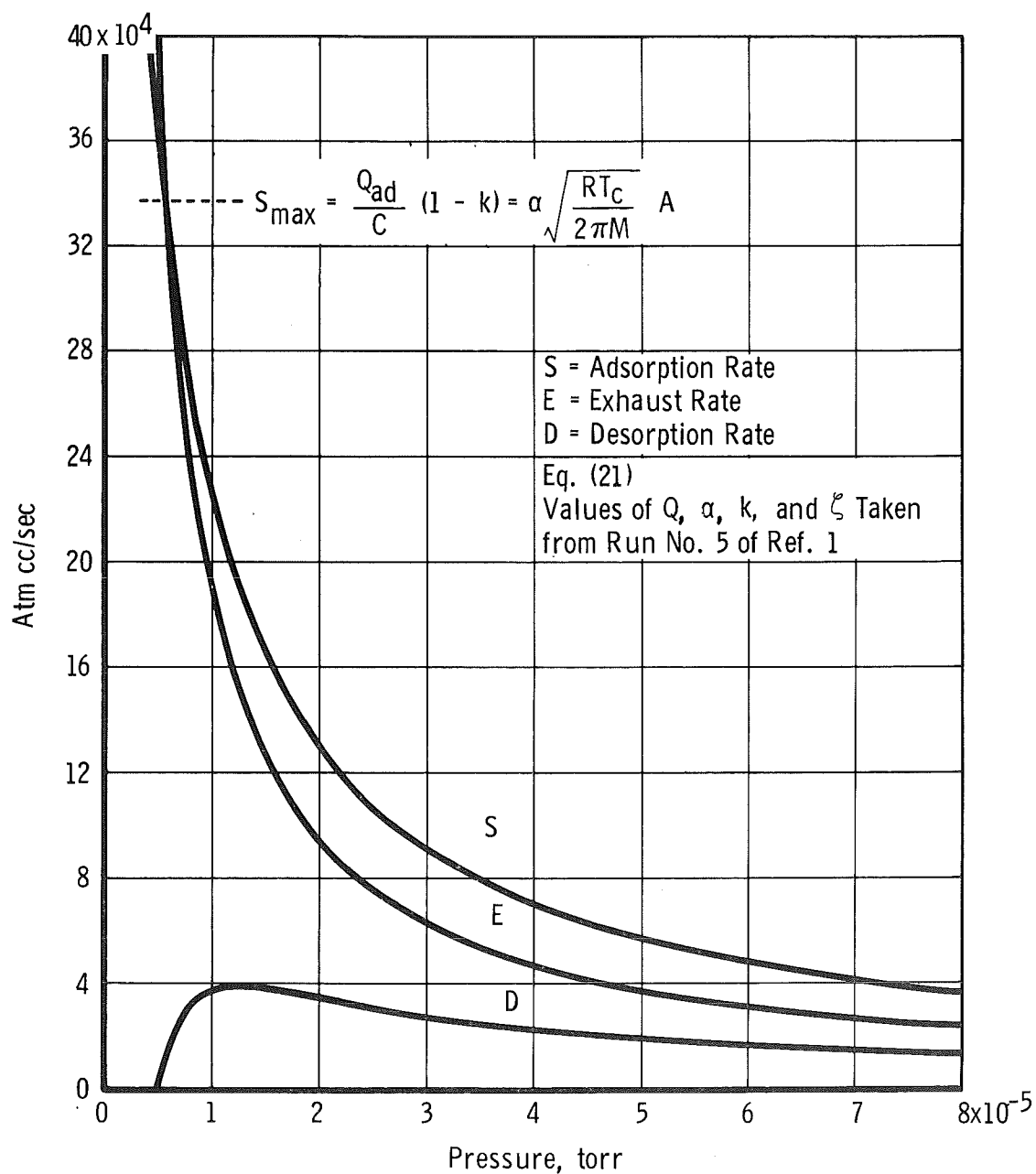


Fig. 11 S, D, and E Curves from Eq. (21)

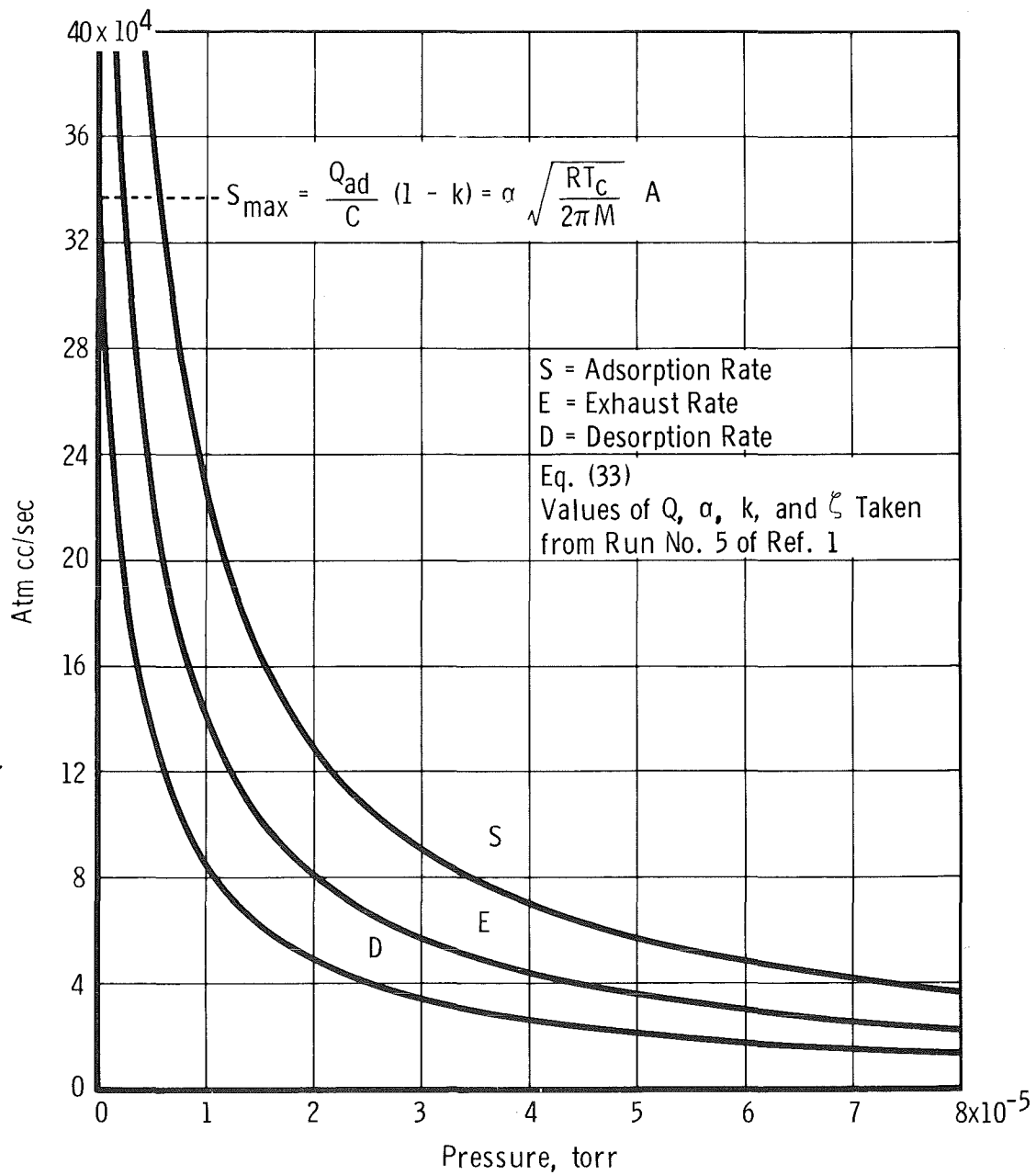


Fig. 12 S, D, and E Curves from Eq. (23)

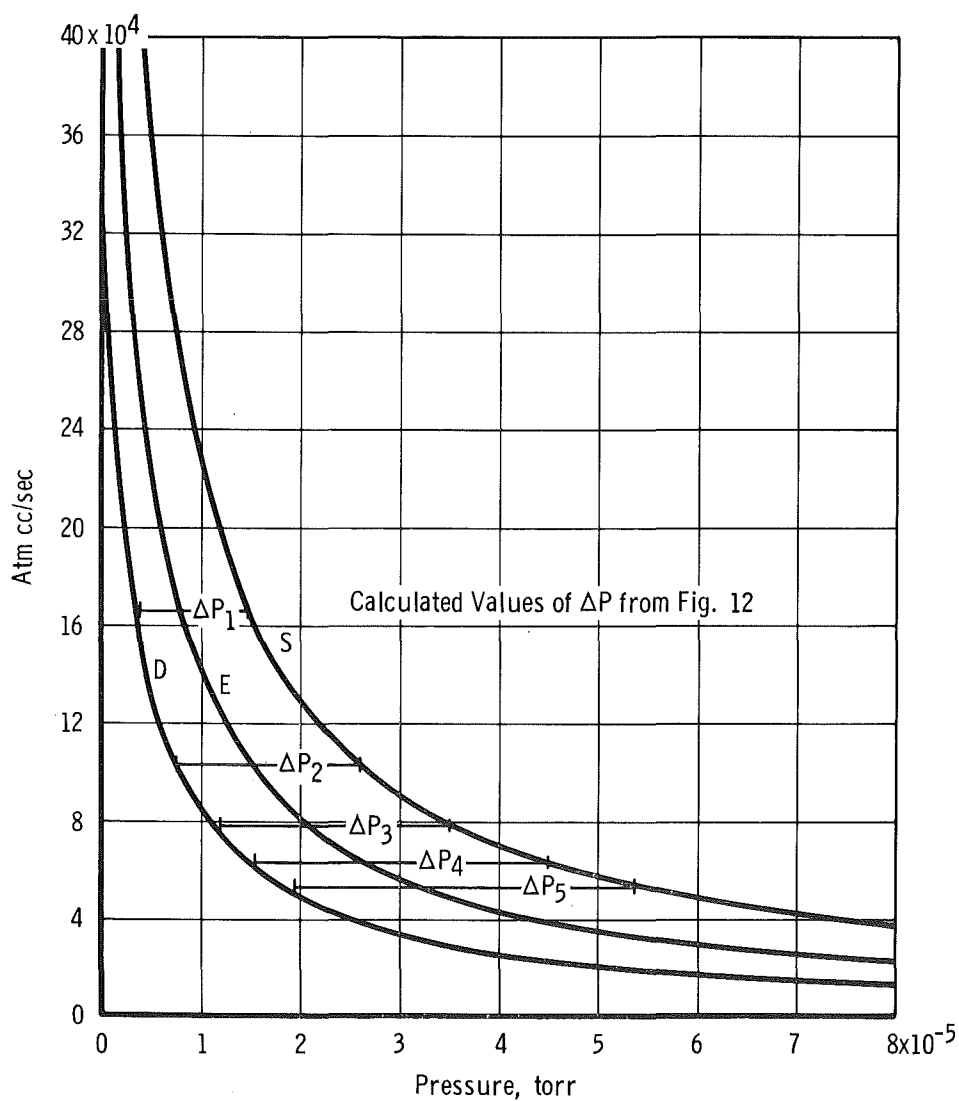
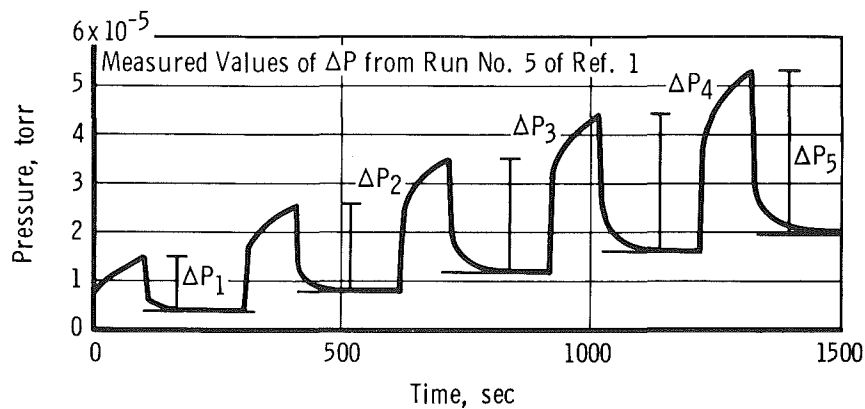


Fig. 13 Comparison of Measured Values of ΔP with Calculated Values of ΔP

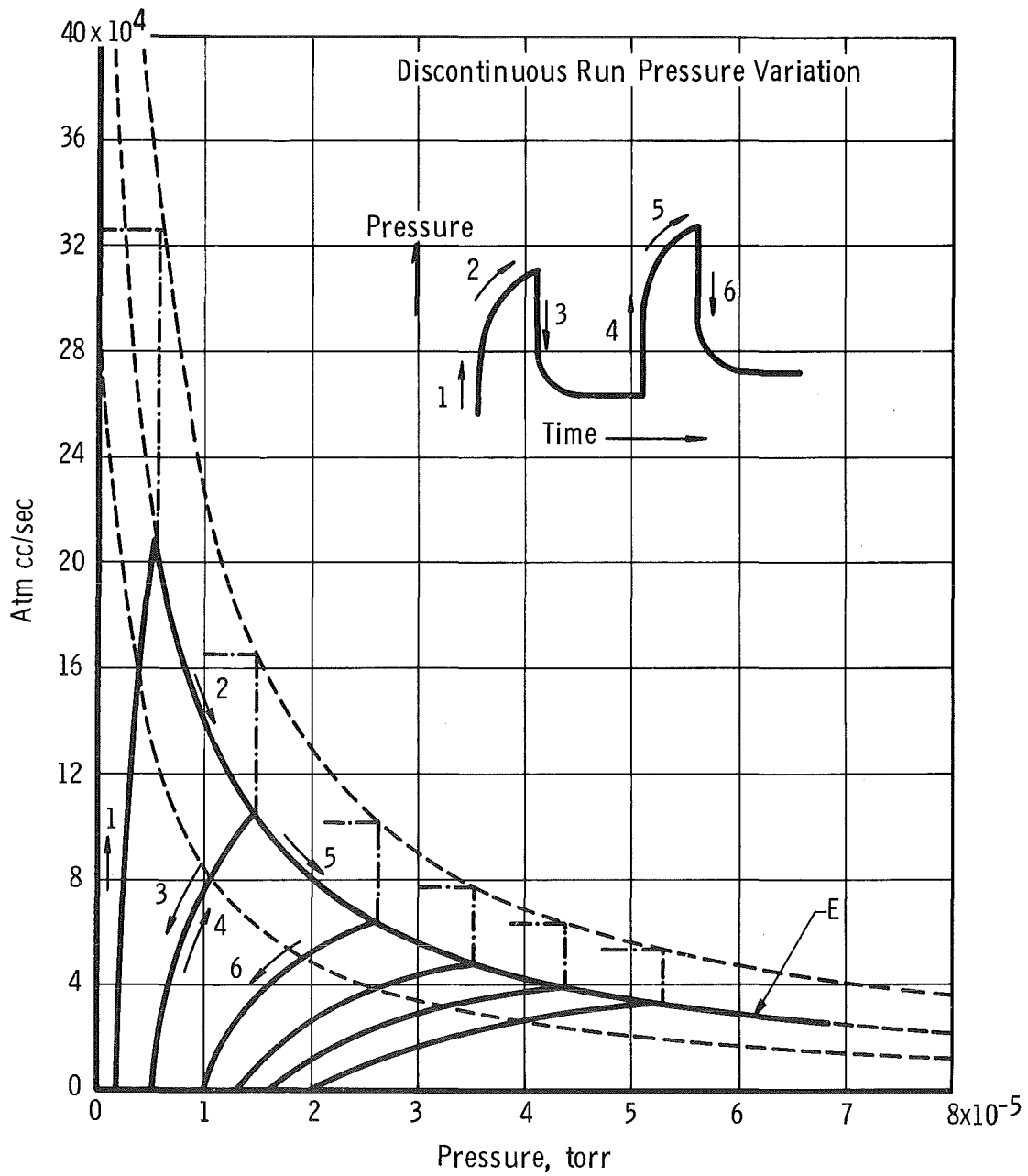


Fig. 14 Variation of E through a Discontinuous Run

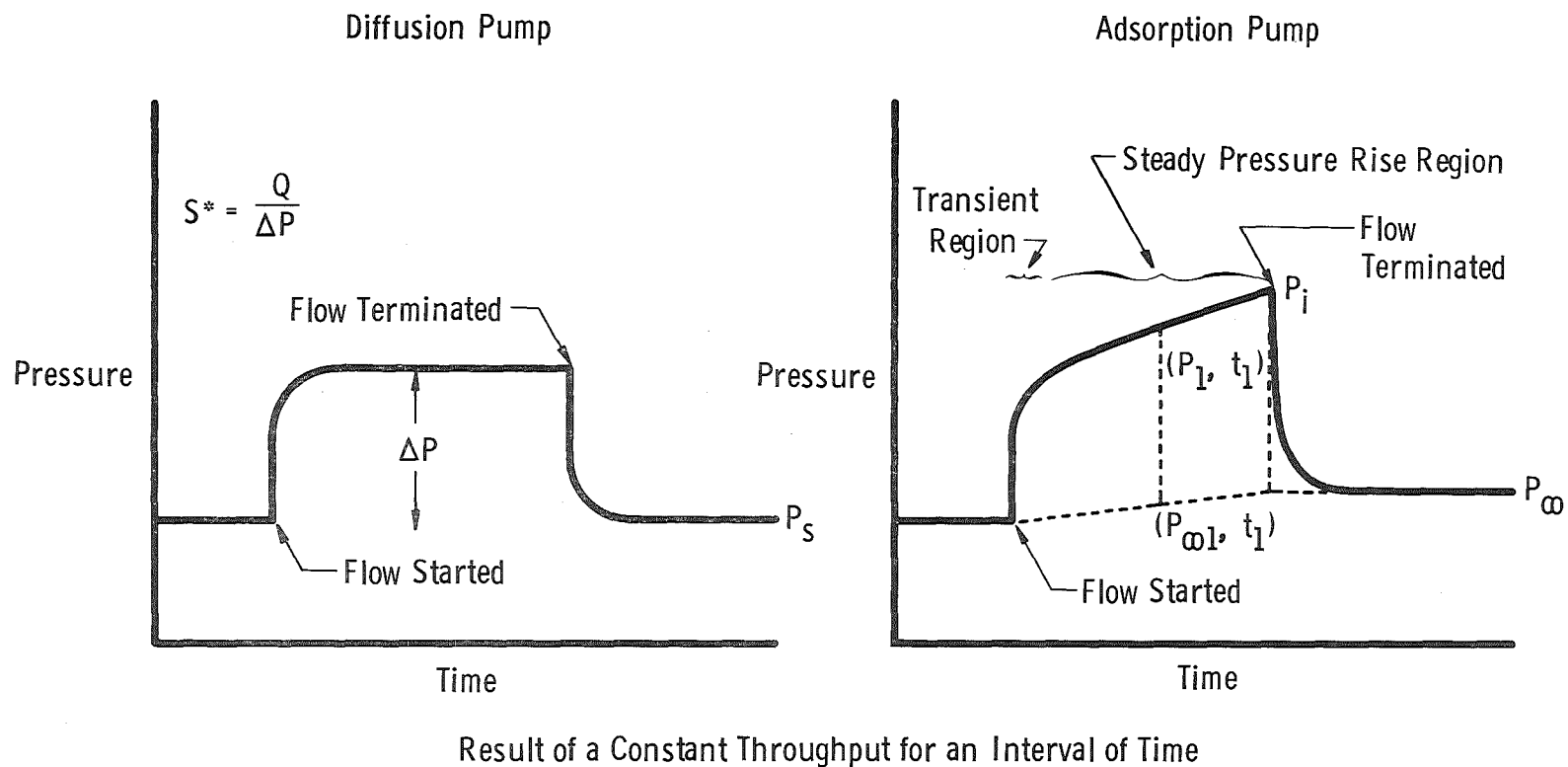


Fig. 15 Explanation of Nomenclature for Pressure-Time Curves of Conventional and Adsorption Pumps